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(54) Title of Invention : Method of determining component concentrations in three-component mixture and method of continuous production of hydrogen fluoride by using the said method.

(57) Abstract

(57) Abstract

A method of quickly and safely determining the component concentrations of a three-component mixture comprising substantially sulfuric acid, hydrogen fluoride and water, which comprises measuring at least one set of three physical quantities of (1) temperature, (2) ultrasonic wave propagation velocity and (3) electric conductivity or viscosity of the three-component mixture and converting the obtained values to the component concentrations on the basis of a working curve representing the relationship between each component concentration of the three-component mixture and the three physical quantities; and a method of continuous production of hydrogen fluoride for controlling a water concentration in the reaction system by using this method.

1...electric conductivity

2...ultrasonic wave propagation velocity
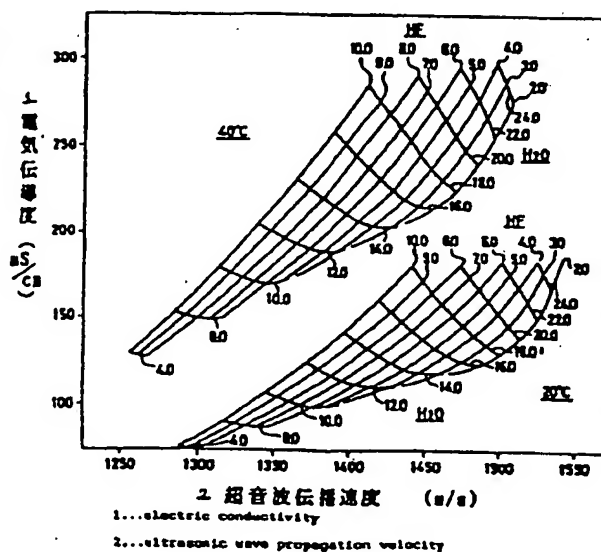
(57) Abstract

Objective of this invention is to provide a quick and safe method of determining the component concentrations in a 3-component mixture with little error and the method of continuous production of hydrogen fluoride by using the said method.

This invention is the method of determining the concentration of each component in the 3-component mixture which substantially consists of sulfuric acid, hydrogen fluoride and water. By this method of determining the concentration of each component in the 3-component mixture, at least one set of the 3 physical quantities, i.e. (1) temperature, (2) ultra sonic wave propagation velocity and (3) electric conductivity or viscosity of the said 3-component mixture, is measured and the values obtained by the measurements are converted to the component concentrations on the basis of the calibration curves which are prepared in advance separately and indicate the relationship between the concentration of each component of the 3-component mixture consisting of sulfuric acid, hydrogen fluoride and water and the above mentioned 3 physical quantities. This invention is also the

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method of continuous production of hydrogen fluoride in which the water concentration in the reaction system is controlled by using the above described method.

Specification

Method of determining component concentrations in three-component mixture and method of continuous production of hydrogen fluoride by using the said method

Field of Technology

This invention is related to the method of determining the concentration of each component in the 3-component mixture which consists substantially of sulfuric acid, hydrogen fluoride and water and to the method of continuous production of hydrogen fluoride by using the said method.

Background of the Technology

The method of determining the concentration of a certain component in the mixture of a plural number of chemical components of known types without the direct measurement, by other means, i.e. indirectly, by a simple procedure, is believed to have a broad range of application. When this is a 2-component mixture, several practically useful methods are known but, when it is a 3-component mixture, an effective method has not existed so far.

Thereupon, for example in the case of determining the concentration of water in a 3-component mixture which contains water, the said 3-component mixture was sampled and the direct determination by Karl Fischer's method has been practiced generally.

However, the method of determining a certain component in such 3-component mixture by direct measurement frequently takes a long time and so it is not suitable in the application which requires the results of measurement fast; also, there is the shortcoming related to the possibility of large error in the measurement.

Furthermore, when a substance which is harmful to human body is contained in such a 3-component mixture, the direct measurement and the sampling work for this are accompanied by hazards at the handling.

Now, hydrogen fluoride is a very important substance that is the raw material in making various fluorine-containing resins and fluorine-containing compounds. Hydrogen fluoride can be obtained industrially by reacting fluorite and sulfuric acid. At the industrial production of hydrogen fluor-

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ide by this reaction, the high boiling point mixture which contains the unreacted sulfuric acid is recycled for reuse without being taken out of the system for disposal.

The method which is used currently in general comprises the following processes.

Thus, it is a method of continuous production of hydrogen fluoride, the method consisting of: the process (1) of reacting the raw material fluorite and the raw material sulfuric acid; the process (2) of separating the crude product obtained from the said process (1) into the low boiling point mixture (a) whose main component is hydrogen fluoride and the high boiling point mixture (b) which contains the unreacted sulfuric acid as the main component and a small portion of hydrogen fluoride and water; the process (3) of refining and obtaining hydrogen fluoride from the said low boiling point mixture (a); the process (4) of adding to the said high boiling mixture (b) an approximately equivalent amount of anhydrous sulfuric acid as the amount of water in it to react with the water to form sulfuric acid and convert all of the water substantially to sulfuric acid and, together with the unreacted sulfuric acid contained in it, returning it to the said process (1) as the raw material sulfuric acid; and the process (5) of supplementing the raw material sulfuric acid to make up the amount necessary in the reaction with the raw material fluorite.

The above said processes are explained in further detail.

In the above described process (1), first, in the kneading and heating process, the raw material fluorite and the raw material sulfuric acid are let in, through the conduit tubes respectively, to the reactor which comprises the kneader and kiln and, by the kneading in the kneader and by the heat treatment in the kiln at 400 ~ 500 deg C, the two are reacted. By this reaction, the fluorite (CaF_2) and the sulfuric acid (H_2SO_4) react by

$$CaF_2 + H_2SO_4 \Rightarrow CaSO_4 + 2HF$$
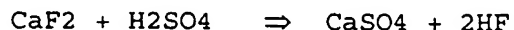
to form hydrogen fluoride. Simultaneously at this time, the minute amount of impurities such as silicon oxide and calcium carbonate which are contained in the raw material fluorite undergo the reactions of

$$SiO_2 + 4HF \Rightarrow SiF_4 + 2H_2O$$
$$CaCO_3 + H_2SO_4 \Rightarrow CaSO_4 + H_2O + CO_2$$
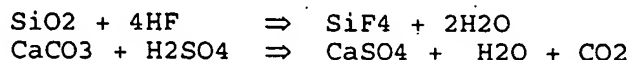
to form water, etc. which is the by-product.

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In order to make the hydrogen fluoride of high purity, a process of removing the unreacted substances and these by-products is necessary.

For this, in the above said process (2), the crude gas which is the reaction product from the said kneading and heating processes is led into the crude gas washing tower and the washing and primary refining treatment of the crude gas is conducted. This crude gas washing tower plays somewhat different roles at the lower section and upper section. Thus, the crude gas at high temperature which is generated from the reaction apparatus is first led into the lowest section of the crude gas washing tower. Here, the high boiling point mixture (b) with the main component of sulfuric acid accumulating in the storage tank installed at the lower side of the crude gas washing tower is pumped into the section which is slightly below the middle of the crude gas washing tower and this is contacted with the said crude gas at high temperature which is coming up, to remove the dust which accompanies the gas from the reaction process. On the other hand, at the upper section of the tower, the hydrogen fluoride in liquid form which was condensed in a later process is let to fall from the tower top and this is contacted with the crude gas which comes up from the lower side of the tower with its dust removed; by the effect of condensation, the high boiling point substance (sulfuric acid, water) is removed and, from the tower top of the said crude gas washing tower, the low boiling point mixture (a) whose main body is hydrogen fluoride is taken out.

Then, in the above said process (3), through the process of refining the low boiling point mixture (a) which was taken out in the above described washing process, the hydrogen fluoride of high purity which is the desired product is obtained.

The sulfuric acid which is contained in the high boiling point mixture (b) which was separated and removed in the above described washing process can be used again in the above described hydrogen fluoride formation reaction for the effective utilization of resource; also, for the prevention of environmental pollution, it is undesirable to discard this. Therefore, the process of recycling this as the raw material sulfuric acid is necessary.

For this, in the above described process (4), there is installed the process which performs the following functions: The high boiling point mixture (b) which is separated by the above described washing process is led to a mixing tank; to this, the anhydrous sulfuric acid (normally in the form of fuming sulfuric acid) is added ; the water which is a by-product is reacted with anhydrous sulfuric acid to form sulfuric acid ; separately, new sulfuric acid is supplement-

ed to make up the substantially total amount of the raw
material sulfuric acid which is needed in the reaction with
the raw material fluorite ; and this is returned to the
kneading and heating process.

In this process, if the amount of water contained is too
much compared to the anhydrous sulfuric acid, water remains
in the raw material sulfuric acid and the reaction is slowed
and there arises the problem of the reaction material
sticking to form bulk and, at the same time, corrosion of
apparatus and piping occurs throughout the whole recycling
process. Therefore, it is necessary to determine accurately
the amount of anhydrous sulfuric acid to be added to the
mixing tank so that the amount of said water would not be
too much, from the amount of water contained in the high
boiling point mixture (b). As an important factor in this,
the concentration of water in the said high boiling point
mixture (b) needs to be determined accurately in the said
process (4).

In the past, for the measurement of this water concentra-
tion, a certain amount of the high boiling point mixture was
sampled at a constant time interval from the conduit tube
of the production apparatus and direct determination was
conducted by Karl Fischer's method.

Such method, however, involved the shortcoming that the
sampling procedure itself was a handling of the hydrogen
fluoride and sulfuric acid which are hazardous materials.
Also, it takes a considerable length of time from the sampl-
ing to the obtaining of the result of measurement and so the
amount of water content could not be known on the real time
and so there was the disadvantage of delay in the adjustment
of the amount of anhydrous sulfuric acid.

Summary of the Invention

In view of the above described current situation, the ob-
jective of this invention is to provide the method of deter-
mining the component concentrations in the 3-component mix-
ture, the method being fast with little error and the work
being safe, and to provide the method of continuous produc-
tion of hydrogen fluoride by using the said method.

The method of this invention is a method of determining
each of the component concentrations in the 3-component mix-
ture which substantially consists of sulfuric acid, hydrogen
fluoride and water and it is the method of determining each
of the component concentrations in the 3-component mixture,
the method being characterized by measuring at least one set
of the 3 physical quantities of (1) temperature, (2) ultra-
sonic wave propagation velocity and (3) electric conducti-

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vity or viscosity of the 3-component mixture and converting
the values of this measurement to the component concentra-
tions on the basis of the calibration curves which express
the relationship between the component concentrations in the
3-component mixture consisting of sulfuric acid, hydrogen
fluoride and water that were prepared in advance.

The measurement of concentration by this invention is,
for example, a method in which the 3-component mixture for
which the component concentrations are to be measured is
maintained at a certain temperature and the ultrasonic wave
propagation velocity and the electric conductivity or visco-
sity are measured and the measured values are converted to
the component concentration on the basis of the said calib-
ration curves.

Also, the method of continuous production of hydrogen
fluoride of this invention which uses the above described
method is characterized as follows: It is a method of con-
tinuous production of hydrogen fluoride, the method consist-
ing of: the process (1) of reacting the raw material fluo-
rite and the raw material sulfuric acid; the process (2) of
separating the crude product obtained from the said process
(1) into the low boiling point mixture (a) whose main compo-
nent is hydrogen fluoride and the high boiling point mixture
(b) which contains the unreacted sulfuric acid as the main
component and a small portion of hydrogen fluoride and
water; the process (3) of refining and obtaining hydrogen
fluoride from the said low boiling point mixture (a); the
process (4) of adding to the said high boiling mixture (b)
an approximately equivalent amount of anhydrous sulfuric
acid as the amount of water in it to react with the water to
form sulfuric acid and convert all of the water substantial-
ly to sulfuric acid and, together with the unreacted sulfur-
ic acid contained in it, returning it to the said process
(1) as the raw material sulfuric acid; and the process (5)
of supplementing the raw material sulfuric acid to make up
the amount necessary in the reaction with the raw material
fluorite. In the above said process (4), the amount of water
contained in the high boiling point mixture (b) is determin-
ed by the application of the above described method of de-
termining, by this invention, the component concentrations
in the 3-component mixture, particularly determining the
concentration of water content.

Brief Description of the Figures

Fig. 1 is the calibration curve of this invention which
was obtained in the Reference Example 1-1 and it expresses
the relationship between the component concentrations within
a certain range of component concentrations in the 3-compo-
nent mixture consisting of sulfuric acid, hydrogen fluoride
and water and the ultrasonic wave propagation rate (m/s) and

electric conductivity (mS/ cm) at 20 deg C and 40 deg C. The set of calibration curves at the upper side is for 40 deg C and the set of at the lower side is for 20 deg C. Also, the numerical values which are attached to each calibration curve indicate the water concentration (wt %) and hydrogen fluoride concentration (wt %).

Fig. 2 is the diagram obtained by eliminating the calibration curves showing the concentration of hydrogen fluoride from Fig. 1 for convenience to facilitate the determination of water concentration.

Fig. 3 is the calibration curve of this invention which was obtained in the Reference Example 1-2. It shows the relationship between the component concentrations within a certain range of component concentrations in the 3-component mixture consisting of sulfuric acid, hydrogen fluoride and water and the ultrasonic wave propagation rate (m/s) and viscosity (cP) at 20 deg C and 40 deg C. The set of calibration curves at the upper side is for 20 deg C and the set of at the lower side is for 40 deg C. Also, the numerical value which are attached to each calibration curve indicate the water concentration (wt %) and hydrogen fluoride concentration (wt %).

Fig. 4 is the diagram obtained by eliminating the calibration curves showing the concentration of hydrogen fluoride from Fig. 3 for convenience to facilitate the determination of water concentration.

Fig. 5 is a schematic diagram showing an example of the reaction apparatus in the method of continuous production of hydrogen fluoride in this invention which is used in Example of Application 2.

The codes indicate the following: ·

1. Kneader; 2. Kiln; 3. Crude gas washing tower; 4. Storage tank; 5. Mixing tank; 19. The means for measuring the ultrasonic wave propagation velocity and the electric conductivity; 20. The means for measuring the ultrasonic wave propagation velocity and the viscosity; 21. The means for feeding the anhydrous sulfuric acid; 23, 26. Flow rate control valves.

Detailed Disclosure of the Invention

In the following, the present invention is described in detail.

First, the method of determining the concentration of each component in the 3-component mixture of this invention

(method of measurement of the component concentration) is explained.

The mixture to which the method of measurement of the component concentrations of this invention can be applied is the 3-component mixture which substantially consists of the 3 components of sulfuric acid, hydrogen fluoride and water. Here, [substantially] means that minute amounts of other components may be contained but that the components which are the measurable objects are only the 3 components of sulfuric acid, hydrogen fluoride and water.

As to the concentrations of the said 3 components in the said mixture, there is no particular limit. However, normally, the concentration range of sulfuric acid 70 ~ 100 wt %, hydrogen fluoride 0 ~ 30 wt %, water 0 ~ 30 wt % is the object. In the method of continuous production of hydrogen fluoride which will be described later in detail, the component concentrations in the 3-component mixture fall in this range.

In the method of measurement of component concentration in this invention, first, the set of 3 physical quantities of (1) temperature, (2) ultrasonic wave propagation velocity, and (3) electric conductivity or viscosity, are measured for the 3-component mixture for which the concentration of each component is known. This is done to obtain the calibration curves in this invention, the curves showing the correlation between the component concentrations of the said 3 components and the 3 physical quantities.

The method of measurements of component concentration of this invention was accomplished for the first time when the present inventors discovered that there is the reproducible correlation between each of the component concentrations in the 3-component mixture and the said 3 physical quantities.

Determination of the component concentrations in a 2-component mixture by the method of ultrasonic wave measurement is known. Thus, in general, the ultrasonic wave propagation velocity in a solution varies with the component concentration and temperature in the solution. Therefore, it is possible to determine the component concentration in a solution by measuring the ultrasonic wave propagation velocity in a solution at a certain temperature.

On the other hand, in a 3-component mixture like the high boiling point mixture (b) in the method of continuous production of hydrogen fluoride, a measurement of the ultrasonic wave propagation velocity at a certain temperature alone gives a large error in determining the concentration and it was found by the investigation of the present inventors that

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the accurate component concentrations can not be measured by the existing method of measuring the ultrasonic wave propagation velocity.

In this invention, as described below in detail, the concentration of water in the 3-component mixture can be determined with a high accuracy.

First, the preparation of above described calibration curves is explained.

Basically, for example, under the atmospheric pressure, for the 3-component mixture of all concentrations in the liquid form, at all temperatures, the set of the other two physical quantities are measured (normally, for the concentration increment of 1 or 2 wt %, measurements are made with the temperature increment of 5 deg C and the physical quantities between those concentrations and temperatures are determined by linear interpolation on the basis of the nearest two values which were measured). Then the measured values of the two physical quantities are plotted on the ordinate and abscissa to obtain the calibration curve.

In the following, description is given on the concentration. But, for the temperature, also, the idea is same.

To obtain the calibration curve, the 3-component mixture of known concentration of each component is prepared. Such 3-component mixture can be prepared, for example, as follows.

Among the component concentrations of the desired 3-component mixture, first the mixed solution of water/ hydrogen fluoride having the desired concentration ratio of water and hydrogen fluoride is prepared. Next, to a prescribed amount of this, the prescribed amount of sulfuric acid is added to prepare a prescribed number of the 3-component mixtures of desired component concentrations.

In this way, a total of 961 types of the 3-component mixtures of sulfuric acid, hydrogen fluoride and water can be prepared, normally with the variation of hydrogen fluoride concentration with an increment of 1 wt % between 0 ~ 30 wt % and the variation of water concentration with an increment of 1 wt % between 0 ~ 30 wt %. For the explanation to be given later, for example, these are named as lot 1, lot 2, - -- lot 961.

To draw accurate calibration curves, for the above mentioned 961 types of 3-component mixtures, 3 samples were prepared for each lot and the 3 physical quantities were measured and their average value was determined.

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The 3-component mixture which is prepared as described above is first set to a constant temperature. In setting the temperature in this manner, the method which is normally conducted is used. For example, the method of dipping the container or cell in a constant temperature tank can be used. As for the above mentioned temperature, preferred temperature range is where the concentrations of the 3 components are not influenced under the atmospheric pressure, i.e. where the mixture is in the liquid state. For example, 15 deg C and 45 Deg C are used.

As to the material of the container or cell, it needs to have resistance to the 3-component mixture.

After setting the temperature as described above, for the above said 3-component mixtures, the ultra sonic wave propagation velocity is measured while the temperature is kept constant. As for the instrument for the measurement of ultrasonic wave propagation velocity, there is no particular restriction as long as it can measure the ultrasonic wave propagation velocity of liquid. Preferred example is the instrument based on the Sing-around method.

The ultrasonic wave propagation velocity which is measured is recorded for each of the lot 1, lot 2, --- lot 961.

Next, in the similar way for the above said 3-component mixtures, electric conductivity is measured while the temperature is kept constant. As for the instrument for measuring the electric conductivity, an example is the one as follows: In a container where an electrically conductive liquid is let to be present, a magnetic field is acted vertically and electrodes are installed to face each other in the direction perpendicular to the direction of the magnetic field and the voltage between the electrodes which are generated by the electromagnetic induction is measured to measure the electric conductivity.

The electric conductivity which is measured is recorded for lot 1, lot 2, --- lot 961.

Based on the two physical quantities obtained here, for example, the ultrasonic wave propagation velocity is plotted on the abscissa and the electric conductivity is plotted on the ordinate to obtain on the graph the collection of 961 points of lot 1, lot 2, --- lot 961.

Measurement of viscosity is conducted by the viscosity measurement instrument in the similar manner as described above while the temperature is kept constant. The measured values obtained are recorded similarly for each lot. As to

the above described viscosity measuring instrument, there is no particular restriction as long as it can measure the viscosity of a liquid.

The two physical quantities of ultrasonic wave propagation velocity and viscosity are plotted in the similar manner as in the above described case of ultrasonic wave propagation velocity and electric conductivity to obtain the collection of points.

These measurements are conducted with 3 samples for each lot and their average value is taken to obtain accurate values of measurements.

The present inventors discovered that, when the points corresponding to the lots for which the amount of water and hydrogen fluoride is constant are connected among the above said collection of points, there is a certain relative relationship at a constant temperature between these two sets of the two physical quantities. The curves obtained in this manner draw the stripe patterns which are mutually similar in parallel.

In the case where the water concentration in the said 3-component mixture is 4.0 ~ 24 wt %, hydrogen fluoride is 2.0 ~ 10 wt % and the remainder is sulfuric acid, the physical quantities which should be measured are preferably the temperature, ultrasonic wave propagation velocity and electric conductivity but, in the case where the water concentration in the said 3-component mixture is 0 ~ 7.0 wt %, hydrogen fluoride is 0 ~ 9.0 wt % and the remainder is sulfuric acid, it is preferred to measure the viscosity in place of electric conductivity among the said items of measurements. So, as for the physical quantities which should be measured, a suitable selection can be made depending on the anticipated concentration range of each of the components contained in the test specimen and the decision can be made as to whether the temperature, ultrasolic propagation velocity should be used or the temperature, ultrasonic wave propagation velocity and viscosity should be used.

Next, explanation is given on the method of determining the component concentrations of a 3-component mixture for which the component concentrations are not clear, by utilizing the calibration curves which were obtained in this manner.

We use a test specimen which is the 3-component mixture but for which all of the concentrations of the said 3 components are not clear. For the said test specimen, at a constant temperature, the above described ultrasonic wave propagation velocity is measured. After this, for the same test

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specimen, at the same temperature, the electric conductivity is measured. From the measured values of the ultrasonic wave propagation velocity and electric conductivity, on the graph where the calibration curves were drawn as described above, the position is fixed as the intersection of the abscissa and ordinate of their values.

The position which was fixed on the graph is checked; if the position is on any of the calibration curves which were obtained as described above or on their intersections, the corresnponding concentrations of water and/ or hydrogen fluoride indicate the concentrations of the water and/ or hydrogen fluoride of the test specimen. In the case where the position of the point determined is not on the line or at the intersection of the calibration curves obtained as above, it is possible to determine the concentrations of water and/ or hydrogen fluoride of the test specimen by proportion from the relationship of the distances between the 2 calibration curves which are parallel and have the said point in between and between the calibration curve and the said point. For example, if the said point is between the calibration of curves of water concentration 10 wt % and 11 wt %, and if [the distance between the said 2 calibration curves] : [the distance between the said point and the calibration curve of 10 wt %] = 10 : 4, the concentration of water of the test specimen is indicated to be 10.4 wt %. In the case of determining the concentration of hydrogen fluoride, the procedure is approximately same as in the above described case of water. Concentration of the sulfuric acid is determined by subtracting the concentrations of water and hydrogen fluoride from 100 wt %.

In the above, the technique of determining the concentration by proportion from the calibration curves was described for the case of concentration. For the case of temperature, also, the entirely same procedure can be conducted.

In this way, from the measured values of 2 physical quantities at a constant temperature, the position of intersection point determined on the graph of calibration curves can be fixed and, from the positional relation of the position and the calibration curves, the concentrations of water, hydrogen fluoride and sulfuric acid of the test specimen can be determined.

In the method of measurements of component concentration of this invention, after preparing the above described calibration curves, the concentrations of water, hydrogen fluoride and sulfuric acid of the test specimen can be determined by measuring the ultrasonic wave propagation velocity and electric conductivity or viscosity at a constant temperature.

Thus, a typical example of the means for determining the component concentration of this invention comprises (1) the means for keeping the test specimen at a constant temperature, (2) the means for measuring the ultrasonic wave propagation velocity, (3) the means for measuring the electric conductivity or the means for measuring the viscosity, and (4) the means for determining the concentrations of water, hydrogen fluoride and sulfuric acid in the test specimen (hereinafter, this is called the [means (M1)]) as described above from the results of measurement in (2) and (3) described above by using the above mentioned calibration curves. As for the means of (4) mentioned above, the procedure can be conducted manually by using the graph of calibration curves as described above but, in order to conduct the treatment accurately and fast, it is preferred to conduct the treatment by using a computer as will be described later in the examples of application. And, on the basis of the information which was treated by the computer, the automatic flow rate control valve can be operated by the common method to automate the control of the increase or reduction of the feed rate of the anhydrous sulfuric acid.

In the following, explanation is given on the method of continuous production of hydrogen fluoride of this invention by using the method of measurements of concentrations of the 3-component mixture which has been described above.

In the method of continuous production of hydrogen fluoride in this invention, the above described method of measurements of component concentrations of this invention is applied to the concentration of water in the high boiling point mixture (b) in the method of continuous production of hydrogen fluoride in the existing technology.

In the method of continuous production of hydrogen fluoride in this invention, the hydrogen floride is produced as follows: The raw material fluorite and the raw material sulfuric acid are kneaded and heated and the crude gas generated from this process is let into the crude gas washing tower. Here, the said crude gas is washed by sequential contact with the high boiling point mixture whose main component is sulfuric acid and with the hydrogen fluoride. By this, the low boiling point mixture whose main body is hydrogen fluoride is taken out from the tower top of the said crude gas washing tower and this is refined to obtain the product. At the same time, the high boiling point mixture which accumulates at the lower section of the above said crude gas washing tower containing sulfuric acid as the main component and containing a small ratio of water and hydrogen fluoride is taken out and, to this, anhydrous sulfuric acid is fed by an approximately equivalent amount for the formation of sulfuric acid by reacting with water, relative to the amount of water contained in the above said high boiling point mix-

ture, to produce sulfuric acid. This anhydrous sulfuric acid can be used as the mixture of the anhydrous sulfuric acid and sulfuric acid normally in the form of the fuming sulfuric acid.

In this invention, measurement of the amount of water contained in the above mentioned high boiling point mixture is conducted by applying the above described method or means for the measurement of component concentrations in this invention. And, on the basis of the results of the measurements, anhydrous sulfuric acid is fed. By this, in this invention, it is possible to measure the above said amount of water on the real time at the desired time interval or continuously without relying on manual work and it is possible to feed and mix the optimal amount of anhydrous sulfuric acid fast and safely.

In this invention, relative to the amount of water in the above said high boiling point mixture (b) as measured by the above described method, an equivalent amount of anhydrous sulfuric acid for forming sulfuric acid by reacting with the water is fed. As to this means of feeding (hereinafrer, this is called [the means (M2)]), there is no particular restriction as long as it is a means which can feed and mix the anhydrous sulfuric acid by the above said equivalent amount relative to the amount of water contained in the above said high boiling point mixture (b) as measured by the above described means (M1); it can be conducted manually or it can be conducted automatically. As for such means (M2), for example the feeding apparatus which is automatically controlled to match the amount of water contained in the above said high boiling point mixture (b) as measured by the above said means (M1) is preferred.

Also, in this invention, it is preferred that the above said means (M2) is controlled by the means which can determine the feed rate of anhydrous sulfuric acid from the results of measurements and calculation by the above said means (M1). As for such means of control, an example is to conduct the control by an electronic computer which computes the equivalent amount of anhydrous sulfuric acid on the basis of the water concentration that is determined by the above said means (M1).

As for the measurement and calcualtion by the above said means (M1), it can be conducted before mixing the anhydrous sulfuric acid to the said high boiling point mixrure (b), or after mixing the anhydrous sulfuric acid to the said high boiling point mixture, or before and after mixing the anhydrous sulfuric acid to the said high boiling point mixture. However, from the view point of optimal control of the sulfuric acid concentration during the production, it is pre- ferred to be conducted before and after the mixing of

anhydrous sulfuric acid to the said high boiling point
mixture.

As to the amount of addition of anhydrous sulfuric acid
to the said high boiling point mixture in this invention, it
is preferably an approximately equal amount as the amount
needed for generating sulfuric acid by the reaction with the
water which is contained in the said high boiling point mix-
ture. If the amount of anhydrous sulfuric acid is less than
the equal amount needed for generating sulfuric acid by the
reaction with the water contained in the said high boiling
point mixture, the unreacted water remains and the reaction
rate drops and the reaction mixture forms bulk or sticks
inside the apparatus and there is the danger of hindering
the smooth proceeding of the reaction of the raw material
sulfuric acid and the raw material fluorite and, at the same
time, corrosion is increased on all piping and the apparatus
which participate in the recycling process such as the kiln
and crude gas washing tower. 1

In other words, the present inventors found out by exper-
ience that, in order to maintain the rate of reaction of
fluorite and sulfuric acid at a high level and to prevent
the bulk formation of the reaction mixture, it is necessary
to maintain the amount of water contained in the raw mater-
ial sulfuric acid below about 5 wt %, preferably below about
3 wt %. But, by following this invention to add the anyhd-
rous sulfuric acid by an amount which is approximately equal
to the amount that is needed in generating sulfuric acid by
the reaction with the water for the amount of water contain-
ed here to the high boiling mixture from the crude gas wash-
ing tower described above, it is possible to maintain the
amount of water in the feed sulfuric acid always below 3 wt
%.

In this invention, as described above, by measuring the
amount of water contained in the said high boiling point
mixture (b) and feeding the necessary amount of anhydrous
sulfuric acid, it is possible to avoid the danger of the
situation in which the amount of the said anhydrous sulfur-
ic acid is too little relative to the said amount of water
and so the said water remains in the raw material sulfuric
acid without reacting with the said anhydrous sulfuric acid
and the smooth occurrence of reaction between the raw mater-
ial sulfuric acid and the raw material fluorite is hindered
and, at the same time, it is possible to avoid the occurren-
ce of the corrosion of apparatus and piping which take part
in the recycle process. Also, it is possible to avoid the
situation in which the amount of said anhydrous sulfuric
acid is too much relative to the amount of said water and,
as the result, the concentration of sulfuric acid as the
impurity in the hydrogen fluoride obtained is high.

In this invention, there is included the process of supplementing sulfuric acid to make up the substantially total amount of the raw material sulfuric acid needed in the reaction with the raw material fluorite. In this process, also, the concentration of water can be determined by the above described method for the purpose of checking or helping the concentration of water.

The Best Mode of Application of the Invention

In the following, the invention is described in further detail by giving examples of application of this invention but this invention is not limited to these examples of application.

Reference Example 1. Preparation of the calibration curves which express the correlations between the component concentrations of the 3-component mixture consisting of sulfuric acid, hydrogen fluoride and water and the following 3 physical quantities.

Reference Example 1-1. The case in which the three physical quantities are the temperature, ultrasonic wave propagation velocity and electric conductivity

The following types of samples of the 3-component mixture of water, hydrogen fluoride and sulfuric acid having different component concentrations were prepared by the above described procedure.

Concentration of water: In the range of 4.0 ~ 24.0 wt %, at the increment of 2.0 wt % ; Concentration of hydrogen fluoride: In the range of 2.0 ~ 10.0 wt % at the increment of 1.0 wt %. These were combined and, in all cases, the remainder was set to be the concentration of sulfuric acid. Thus, 90 types of samples were prepared and, for each type of the sample, 3 same samples were made (total 270 samples).

Each of the samples which were obtained as described above was placed in an acid-resistant vessel or a cell which was kept at 40 deg C and the ultra sonic wave propagation velocity (by using Model UVM-2 made by Cho-onpa Kogyo K. K., at 2MHz) and electric conductivity (by the instrument for measuring electric conductivity) were measured. For the numerical values obtained, the average value of 3 pieces was determined. The results are shown in Table 1. In the table, the numerical values at the upper step are the ultrasonic wave propagation velocity (m/s) and the numerical values at the lower step are electric conductivity (mS/ cm).

The measured values obtained were plotted for each constant temperature with the ultrasonic wave propagation velocity on the abscissa and with the electric conductivity on the ordinate on the graph as shown in Fig. 1. The case in which a certain relation could not be obtained was not plotted (also, this was not recorded in the table).

The temperature at the measurement was changed to 20 deg C. Other than this, the same procedure as describe above was followed. The results obtained are shown in Table 2 and in Fig. 1.

Also, in Fig. 1 which was obtained, only the calibration curve showing the concentration of water was kept for convenience to obtain Fig. 2.

Reference Example 1-2. The case in which the 3 physical quantities are temperature, ultrasonic wave propagation velocity and viscosity

Concentration of water: In the range of 0.0 ~ 7.0 wt %, at the increment of 1.0 wt % ; Concentration of hydrogen fluoride: In the range of 0.0 ~ 9.0 wt % at the increment of 1.0 wt %. These were combined and, in all cases, the remainder was set to be the concentration of sulfuric acid. Thus, 80 types of samples were prepared and, for each type of the sample, 3 same samples were made (total 240 samples).

Each of the samples which were obtained as described above was placed in an acid-resistant vessel or a cell which was kept at 40 deg C and the ultra sonic wave propagation velocity (by using Model UVM-2 made by Cho-onpa Kogyo K. K., at 2MHz) and viscosity (by instrument for measuring viscosity) were measured. For the numerical values obtained, the average value of 3 pieces was determined. The results are shown in Table 3. In the table, the numerical values at the upper step are the ultrasonic wave propagation velocity (m/s) and the numerical values at the lower step are viscosity (cP).

The measured values obtained were plotted for each constant temperature with the ultrasonic wave propagation velocity on the abscissa and with the viscosity on the ordinate on the graph as shown in Fig. 3.

The temperature at the measurement was changed to 20 deg C. Other than this, the same procedure as describe above was followed. The results obtained are shown in Table 4 and in Fig. 3.

Also, in Fig. 3 which was obtained, only the calibration curve showing the concentration of water was kept for convenience to obtain Fig. 4.

Table 1.
A. Concentration of hydrogen fluoride (wt);
B. Concentration of water (wt %)

表 1

		フッ化水素の濃度　（重量%)								
		2	3	4	5	6	7	8	9	1 0
水の濃度（重量%）	4	— —	— —	— —	— —	— —	— —	1266.8 126.7	1260.2 127.8	1255.0 129.0
	8	— —	— —	— —	— —	1308.8 149.7	1306.3 149.5	1297.5 150.6	1290.6 152.3	1283.8 154.0
	1 0	— —	— —	1363.8 176.1	1352.5 171.6	1342.5 169.9	1333.8 171.3	1326.3 175.0	1318.8 175.6	1311.3 179.0
	1 2	— —	— —	1340.0 192.0	1328.8 189.0	1369.4 191.5	1361.7 194.6	1354.0 197.3	1344.4 201.1	1336.3 205.1
	1 4	— —	1450.0 202.8	1411.3 204.8	1403.1 206.6	1394.4 210.6	1386.3 215.6	1378.4 221.0	1369.4 225.6	1361.1 230.7
	1 6	1455.0 215.0	1442.5 216.1	1432.5 219.9	1423.8 225.6	1415.6 231.3	1409.4 238.1	1400.9 244.9	1392.5 252.0	1383.8 258.5
	1 8	1468.1 225.0	1458.4 230.8	1450.1 236.9	1443.4 246.1	1435.8 254.0	1427.5 260.8	1421.3 263.6	1413.8 276.9	1406.3 286.4
	2 0	1483.5 238.9	1473.8 248.1	1467.5 256.9	1459.6 265.7	1453.5 275.0	1446.0 283.2	1438.8 291.5	— —	— —
	2 2	1493.8 255.5	1487.5 266.7	1481.9 277.2	1475.6 286.9	1468.8 296.0	— —	— —	— —	— —
	2 4	1503.8 276.3	1499.0 287.7	1492.7 299.2	— —	— —	— —	— —	— —	— —

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Table 2
A. Concentration of hydrogen fluoride (wt);
B. Concentration of water (wt %)

表 2

		フッ化水素の濃度　　（重量%）								
		2	3	4	5	6	7	8	9	1 0
水の濃度（重量%）	4	− −	− −	− −	− −	− −	− −	1300.2 75.0	1293.8 76.0	1292.4 77.2
	8	− −	− −	− −	− −	1337.4 88.6	1337.2 89.1	1329.8 89.2	1325.1 90.3	1316.9 98.0
	1 0	− −	− −	1400.2 100.5	1384.5 100.1	1376.5 100.0	1366.1 101.8	1359.8 103.2	1352.2 105.1	1343.0 107.4
	1 2	− −	− −	1421.7 110.9	1410.7 110.8	1402.4 112.5	1394.5 114.4	1384.5 116.5	1378.0 120.5	1370.0 125.2
	1 4	1459.5 118.2	1454.8 117.8	1444.0 119.3	1433.3 121.0	1426.2 125.1	1417.9 129.1	1409.8 133.0	1402.3 133.8	1394.5 141.8
	1 6	1485.7 122.7	1473.8 125.2	1464.9 129.0	1453.8 132.6	1445.7 138.4	1439.1 143.8	1430.5 148.6	1425.0 154.6	1417.0 160.8
	1 8	1499.8 129.3	1490.5 134.7	1481.0 140.3	1474.6 146.6	1467.3 152.8	1460.4 158.5	1453.0 164.9	1445.7 172.3	1437.7 179.7
	2 0	1512.5 139.2	1504.4 146.0	1497.6 153.2	1489.9 160.5	1483.7 166.8	1476.8 175.3	1471.1 181.1	− −	− −
	2 2	1523.2 151.7	1516.1 160.5	1510.8 167.6	1504.2 175.9	1499.2 182.8	− −	− −	− −	− −
	2 4	1532.3 166.7	1526.8 176.7	1521.4 184.3	− −	− −	− −	− −	− −	− −

B

20

Table 3
A. Concentration of hydrogen fluoride (wt);
B. Concentration of water (wt %)

表3

A HF

β H2O

		水の濃度 （重量%）							
		0	1	2	3	4	5	6	7
フッ化水素の濃度 （重量%）	0	1282.9 13.54	1305.7 12.31	1327.9 11.34	1349.6 10.69	1369.6 10.39	1389.0 10.33	1408.3 10.46	1428.3 10.91
	1	1282.1 12.04	1303.8 11.37	1325.4 10.59	1345.8 10.16	1365.8 9.92	1384.2 9.84	1401.7 9.85	1417.9 10.00
	2	1279.8 10.74	1301.0 10.31	1322.3 9.92	1343.0 9.54	1361.7 9.43	1378.3 9.28	1395.0 9.12	1409.5 9.21
	3	1276.5 9.62	1298.9 9.49	1319.6 9.17	1339.2 9.08	1357.7 8.88	1372.6 8.70	1389.2 8.57	1401.7 8.39
	4	1272.5 8.49	1295.8 8.54	1316.3 8.47	1335.0 8.37	1354.0 8.27	1368.4 8.14	1382.5 7.84	1394.6 7.66
	5	1268.2 7.52	1292.1 7.71	1312.5 7.79	1332.1 7.77	1349.5 7.70	1363.8 7.54	1377.5 7.19	1388.3 6.96
	6	1263.2 6.58	1288.3 6.87	1308.5 7.02	1327.7 7.11	1344.8 7.10	1359.2 6.84	1373.3 6.57	1382.9 6.18
	7	1256.8 5.85	1281.6 6.11	1304.2 6.33	1323.6 6.42	1341.1 6.40	1355.4 6.21	1368.3 5.89	1378.7 5.63
	8	1250.8 5.14	1275.8 5.48	1299.7 5.67	1318.3 5.75	1337.1 5.70	1351.7 5.56	1364.2 5.34	1375.8 4.99
	9	1244.7 4.65	1269.8 4.87	1294.9 5.01	1313.8 5.08	1333.3 5.00	1348.7 5.10	1362.1 4.68	1372.1 4.47

m/s cP

Table 4
A. Concentration of hydrogen fluoride (wt);
B. Concentration of water (wt %)

表 4

		水の濃度　（重量%）							
		0	1	2	3	4	5	6	7
フッ化水素の濃度　（重量%）	0	1259.2 26.61	1281.3 24.40	1302.5 22.89	1322.9 21.73	1343.3 21.13	1362.5 21.18	1383.3 21.68	1402.9 22.71
	1	1255.8 24.14	1277.5 22.75	1299.2 21.67	1319.6 20.96	1338.8 20.54	1357.1 20.55	1373.3 20.90	1391.7 21.51
	2	1252.5 21.69	1275.0 21.08	1295.0 20.50	1315.8 20.05	1333.8 19.84	1350.0 19.86	1365.4 19.93	1380.0 20.28
	3	1248.8 19.78	1270.4 19.48	1292.5 19.29	1311.3 19.13	1327.9 19.10	1345.0 18.99	1358.3 18.99	1371.7 18.99
	4	1244.2 17.82	1266.3 17.92	1288.3 17.99	1305.8 18.08	1324.0 18.02	1339.6 18.00	1352.1 17.85	1365.8 16.37
	5	1238.8 16.11	1262.5 16.54	1283.3 16.78	1302.3 16.89	1318.9 17.01	1335.0 16.93	1346.7 16.71	1359.2 16.38
	6	1234.2 14.32	1257.5 15.16	1278.3 15.47	1298.7 15.68	1315.4 15.70	1330.8 15.62	1342.1 15.41	1353.8 15.01
	7	1232.5 13.46	1251.7 13.91	1274.2 14.20	1293.7 14.35	1310.4 14.35	1327.0 14.30	1338.7 14.05	1350.0 13.62
	8	1222.1 12.38	1246.7 12.72	1268.3 12.86	1289.2 12.89	1306.3 12.89	1322.9 12.75	1336.7 12.55	1348.7 12.17
	9	1215.0 11.53	1240.0 11.57	1263.3 11.50	1283.9 11.41	1302.8 11.31	1320.1 11.19	1334.6 11.04	1348.6 10.78

(upper value: m/s, lower value: cP)

Example of Application 1. Measurement of water concentration
in the 3-component mixture consisting of sulfuric acid, hyd-
rogen fluoride and water by using the calibration curves
which were obtained in Reference Example 1.

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Example of Application 1-1. The case of using the calibration curves which were drawn in Fig. 1

At the temperature of 40 deg C, concentration of water in the mixed acid of hydrogen fluoride and sulfuric acid was measured. As for the sample, the one which is shown in Table 1 was used as the test specimen; in this mixed acid, sulfuric acid concentration was 73 ~ 86 wt %, hydrogen fluoride concentration was 2 ~ 10 wt % and the remainder was water. Measurements of ultrasonic wave propagation velocity (m/s) and the electric conductivity (mS/ cm) were made 2 times for each sample and their average value was taken. From this value, the conversion calculation was conducted manually on the basis of the calibration curves of Fig. 1 and the result is shown in Table 5 as the concentration of water.

From Table 5, it was clarified that, by the method of this invention, concentration of water can be determined with high accuracy. The numerical value in (   ) in Table 5 indicates the actual wt % of water.

Example of Application 1-2. The case of using the calibration curves which were drawn in Fig. 3.

By the same method as in Example of Application 1-1, for the test specimen in which the sulfuric acid, hydrogen fluoride and water (shown in the parentheses) had the concentrations shown in Table 6, at 20 deg C, their ultrasonic wave propagation velocity (m/s) and viscosity (cp) were measured. The measurements were made two times for each specimen and the average value was calculated and, from the value, on the basis of the calibration curves which were drawn in Fig. 3, manual procedure was used as mentioned before to calculate the concentration of the water and the results were as shown in Table 6. As in Table 5, from Table 6, also, it was found that the concentration of water can be determined with good accuracy.

Table 5
A. Sulfuric acid (wt %); B. Hydrogen fluoride (wt %); C.
Electric conductivity (mS/ cm); D. Ultrasonic wave propaga-
tion velocity (m/ s); E. Water (wt %)

表 5

H_2SO_4 — HF

B. フッ化水素 (重量%)		A. 硫酸 (重量%)					
		73	75	78	81	84	86
10	C (電気伝導度 mS/cm)	271	240	198	163	—	—
	D (超音波伝搬速度 m/s)	1394.4	1368.1	1328.8	1293.7	—	—
	E (水 重量%)	16.9 (17)	14.6 (15)	11.5 (12)	8.7 (9)	—	—
7	C (電気伝導度 mS/cm)	279	254	223	185	153	—
	D (超音波伝搬速度 m/s)	1443.1	1423.1	1393.7	1351.9	1313.8	—
	E (水 重量%)	19.5 (20)	17.4 (18)	14.6 (15)	11.2 (12)	8.6 (9)	—
4	C (電気伝導度 mS/cm)	290	259	231	210	187	174
	D (超音波伝搬速度 m/s)	1487.2	1462.2	1443.3	1417.7	1384.8	1359.2
	E (水 重量%)	23.1 (23)	20.2 (21)	17.3 (18)	14.6 (15)	11.8 (12)	9.8 (10)
2	C (電気伝導度 mS/cm)	—	261	238	224	—	—
	D (超音波伝搬速度 m/s)	—	1496.3	1479.3	1465.2	—	—
	E (水 重量%)	—	22.5 (23)	19.7 (20)	17.7 (17)	—	—

Legend:
C 電気伝導度 (mS/cm)	D 超音波伝搬速度 (m/s)
E 水 (重量%)	

(handwritten annotations: "% abs err = 2.4 / 2.9 permissible error"; circled values 8.7 (9) and 8.6 (9))

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Table 6
A. Sulfuric acid (wt %); B. Hydrogen fluoride (wt %); C.
Electric conductivity (mS/ cm); D. Ultrasonic wave propaga-
tion velocity (m/ s); E. Water (wt %); F. Viscosity (cp)

表6

B フッ化水素 (重量%)	硫酸 (重量%) A				
	86	89	92	95	97
8	5.31 / 1369.4 / 5.9 (6)	5.65 / 1263.5 / 2.7 (3)	—	—	—
6	—	6.73 / 1364.7 / 5.2 (5)	7.01 / 1262.4 / 2.1 (2)	—	—
4	—	7.71 / 1425.3 / 6.9 (7)	8.27 / 1344.2 / 3.9 (4)	8.55 / 1236.5 / 1.1 (1)	—
2	—	—	9.19 / 1431.8 / 6.0 (6)	9.69 / 1318.8 / 2.7 (3)	10.33 / 1244.7 / 0.9 (1)

F 粘度 (cp)	超音波伝伝速度 (m/ s) D
E 水 (重量%)	

Example of Application 2. Method of continuous production of hydrogen fluoride.

The apparatus shown in Fig. 5 was used.

The pulverized raw material fluorite was let into the kneader through the conduit tube 11. The raw material sulfuric acid was let into the kneader through the conduit tubes 12, 13. In the kneader 1, the raw material fluorite and the raw material sulfuric acid which were let in were mixed and the reaction was initiated. Further, the reaction mixture was let into the kiln 2 adjacent to the kneader 1 and, by a heat treatment at about 400 ~ 500 deg C,, the reaction was accelerated to obtain the crude gas which contained the sulfuric acid (A) which was used as the raw material and was remaining unreacted, the hydrogen fluoride (B) which is a product, and the water (C) which was generated by the reaction of the impurities that were present by a minute amount in the raw material fluorite. This crude gas was accompanied by the dust which is the various types of minute solid particles (d) which were generated as the re-sult of reaction.

The said crude gas which was generated in the kneader 1 and kiln 2 was led to the lowest section of the crude gas washing tower 3 through the conduit tube 14 and hydrogen fluoride was let in from the tower top for the washing process. The washing by the said hydrogen fluoride was conducted as follows: The hydrogen fluoride which is the product obtained in the crude gas washing tower 3 was led to the condenser through the conduit tube 18 and a part of it was cooled and condensed; this cooled and condensed hydrogen fluoride was returned to the crude gas washing tower 3 through the conduit tube 17 for the washing.

By cooling the said crude gas in the process of washing in the crude gas washing tower 3, the high boiling point mixture (b) containing the main component of sulfuric acid (A) and small ratio of hydrogen fluoride (B) and water (C) is liquefied and this drops to the lower section of the crude gas washing tower 3 and is stored in the storage tank 4. After separating the said high boiling point mixture (b), the remaining product of the low boiling point mixture (a) in which hydrogen fluoride is the main body was obtained through the conduit tube 18. The low boiling point mixture (a) contained, in addition to the hydrogen fluoride, other low boiling point gas components such as SiF_4, SO_2, and CO_2, etc. This was refined further by a known refining method to obtain the hydrogen fluoride of high purity.

The high boiling point mixture (b) stored in the storage tank 4 was cycled to the recycle process by the pump 22 installed in the storage tank through the conduit tube 15. At

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this time, by adjusting the flow rate control valve 23 installed at the conduit tube 15, a part of it was led from the middle of the crude gas washing tower 3 to the lower section by the conduit tube 24 and this was let to fall as a shower to contact with the crude gas at high temperature rising from below. By this contact, the dust (D) which is contained in the crude gas by a considerably large amount was arrested and returned to the storage tank 4. At the same time, the said high boiling point mixture (b) in the storage tank 4 was let into the mixing tank 5 through the conduit tubes 15, 25. On the other hand, concentration of the said water (C) contained in the said high boiling point mixture (b) was determined by the means (M1) and, by the means (M2) for feeding the necessary amount of anhydrous sulfuric acid (B), feeding to the mixing tank 5 was conducted through the conduit tube 16. Further, separately, fresh sulfuric acid was let into the mixing tank 5, with the flow rate controlled by the flow rate control valve 26, through the conduit tube 12.

As for the means M1 (19), the Model-50 made by Fuji Kogyosha was used and, as for the means M1 (20), the Model-70 made by Fuji Kogyosha was used, respectively. The latter was used mainly for checking whether the concentration of water in the conduit 13 was proper or as an auxiliary system in the measurement of the water concentration.

In these means (M1), the instrument for measuring the temperature, the instrument for measuring the ultrasonic wave propagation velocity and the instrument for measuring the electric conductivity or the instrument for measuring the viscosity are put in a unified system and it consists of the specially fabricated apparatus which operates by the computer control. In the computer, there is stored the program which can convert the 3 physical quantities from the said instruments for the measurements to the concentration of water (or hydrogen fluoride) on the basis of the data of the calibration curves that express the relationship between the component concentrations of the 3-component mixture and the 3 physical quantities which were memorized in advance.

The means (M2) and the flow rate control valve 26 are interconnected to each other by the common method to make the automatic control possible. In response to the amount of the anhydrous sulfuric acid which was added by the means (M2), the amount of sulfuric acid which is let in from the conduit tube 12 is adjusted. Thus, there is established a control system of the common method which controls the necessary amount of sulfuric acid as a whole.

For the above described means (M2), the ultrasonic transmitter of the instrument for measuring the ultrasonic wave propagation velocity, the transmitter of the instrument

for measuring electric conductivity and the ultrasonic transmitter of the instrument for measuring viscosity were installed at the required positions in the production plant; separately in the room of instrument installation, the apparatus for the transformation of electric signals from these transmitters was installed and the transmitters and the transformaion apparatus were connected by conductive wires.

Using the above described apparatus, by using 2250 kg/ Hr of the raw material fluorite and 3022 kg/ Hr of the raw material sulfuric acid, the continuous production of 1125 kg/ Hr of hydrogen fluoride was conducted. The concentration of water in the high boiling point mixture (b) generated from the kiln was about 14.7 wt %. To these, 252 kg/ Hr of anhydrous sulfuric acid and 648 kg/ Hr of sulfuric acid were added as 900 kg/ Hr of the 28 % fuming sulfuric acid and, further, 1480 kg/ Hr of sulfuric acid was supplemented.

Applying the above described method of measuring the concentration of water, the operation was continued for about 30 days under the same conditions and, in the result, the water content in the raw material sulfuric acid which is fed to the kiln was maintained to a fluctuation within +2.5 wt % and no troubles occurred.

Possibility of Utilization in Industry

The method of determining the component concentrations in the 3-component mixture of this invention can measure the concentration of water in the 3-component mixture fast with high accuracy. Also, in the method of continuous production of hydrogen fluoride of this invention by using this method, production of hydrogen fluoride can be conducted very safely and with good efficiency.

Claims of the Patent

1. Method of determining the component concentrations in the 3-component mixture, the method being characterized as follows:

This is a method of determining the component concentrations in the 3-component mixture which consists substantially of sulfuric acid, hydrogen fluoride and water;

At least 1 set of the 3 physical quantities, i.e. (1) the temperature, (2) ultrasonic wave propagation velocity and (3) electric conductivity or viscosity, of the 3-component mixture is measured;